

**Development of a
fast, urban chemistry
metamodel**

J. B. Cohen and
R. G. Prinn

Development of a fast, urban chemistry metamodel for inclusion in global models

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A reduced form metamodel has been produced to simulate the effects of physical, chemical, and meteorological processing of highly reactive trace species in urban areas, which is capable of efficiently simulating the urban concentration, surface deposition, and net export flux of these species. A polynomial chaos expansion and the probabilistic collocation method have been used to develop the metamodel, and its coefficients, so that it is applicable under a broad range of present-day and future conditions. The inputs upon which this metamodel have been formed are based on a combination of physical properties (average temperature, diurnal temperature range, date, and latitude), anthropogenic properties (patterns and amounts of emissions), and the nature of the surrounding environment (background concentrations of species). The metamodel development involved using probability distribution functions (PDFs) of the inputs to run a detailed parent chemical and physical model, the Comprehensive Air Quality Model with Extensions (CAMx), thousands of times. Outputs from these runs were used in turn to both determine the coefficients of and test the precision of the metamodel, as compared with the detailed parent model. It was determined that the deviations between the metamodel and the parent mode for many important species (O_3 , CO, NO_x , and black carbon (BC)) were found to have a weighted RMS error less than 10% in all cases, with many of the specific cases having a weighted RMS error less than 1%. Some of the other important species (VOCs, PAN, OC, and sulfate aerosol) usually have their weighted RMS error less than 10% as well, except for a small number of cases. In these cases, the complexity and non-linearity of the physical, chemical, and meteorological processing is too large for the third order metamodel to give an accurate fit. Finally, sensitivity tests have been performed, to observe the response of the 16 metamodels (4 different meteorologies and 4 different urban types) to a broad set of potential inputs. These results were compared with observations of ozone, CO, formaldehyde, BC, and PM_{10} from a few well observed urban areas, and in most of the cases, the output distributions were found to be within ranges of

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the observations. Overall, a set of efficient and robust metamodels have been generated which are capable of simulating the effects of various physical, chemical, and meteorological processing, and capable of determining the urban concentrations, mole fractions, and fluxes of species, important to human health and the global climate.

1 Introduction

Urban regions have high concentrations of species which are harmful to human health, have a direct or indirect impact on the atmosphere's radiative flux balance, and alter the land's ability to uptake carbon. Furthermore, urban regions account for a large and increasing fraction of the Earth's total population and anthropogenic emissions. However, modeling the effects of urban areas on the processing and export of anthropogenic emissions is not straightforward. Urban areas are not easily categorized in a simple or straight forward manner; they are located in regions of diverse geography and meteorology, they have non-constant emissions which are based on technological, economic, and political factors, and they exhibit strongly non-linear processing of primary anthropogenic pollutants. For these reasons, urban areas account for a large amount of the variability and uncertainty in the global atmospheric spatial and temporal distributions of primary and secondary anthropogenic pollutants.

Of the many substances emitted or processed in urban areas, those having a large percentage of their global emissions, production, or destruction occurring in urban regions, those having a large impact on the global radiative balance, or those having concentrations in urban areas sufficient to affect human health, are the focus in this paper. These species are typically heterogeneously distributed over space and time within single urban regions, as well as between different urban regions, due to non-linear chemical and physical processing, differences in local and regional meteorology, and differences in local emissions. To address this level of complexity, properties of urban areas relating to geography, physics, chemistry, and human activity will have to be addressed at both the local and global scale.

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Global chemistry and climate models, in general, use a spatial resolution which is much too coarse to resolve the spatial scales of real urban regions. This in turn requires that these models use, compute, or predict aggregated data or data on large spatial and temporal scales, and then use this data to approximate the desired variables on the urban temporal and spatial scales. Therefore, physical variables which control the system, the concentrations of trace species, and human factors such as primary anthropogenic emissions pertaining to the urban system are derived, for the entire urban area and its environs (a “dilution” approach). Because of this, many of the variables provided at the grid scales of global models are approximations that are not valid or appropriate for use on urban spatial and temporal scales.

In order for a parameterization of urban processing to be used in a global general circulation or chemical transport model, it must be capable of computing the concentrations of important trace species within a given urban area, and the fluxes of these species to the coarser global scale grids from the urban scale grids and back again. Additionally, the parameterization must be computationally efficient and yet still be flexible enough to simulate the highly variable emissions, upwind conditions, geography, and relevant economic and human factors found in urban areas, both for the present and into the near future.

To be computationally efficient, the parameterization will need to have its variables limited to those which are most important in accounting for the non-linear processing of the most important trace species and processes. Some of the specific variables to consider include: the emissions of critical chemical species, the specific temporal and spatial distributions of the emissions, the time of the year, the geographic location, the surface conditions, the elevation, the amounts of rainfall and cloudiness, the horizontal and vertical circulation, the local temperature, the upwind concentrations of the species interacting within the urban area, the amount of sunlight, the relative humidity, and the atmospheric liquid water content. At a minimum, such variables must be known both in the urban area and at its boundaries, as a function of the time of day. In addition to this, since export from one urban area can greatly impact a neighboring urban areas

properties, it is important to know where urban areas are located in relation to each other.

The parameterization must be capable of capturing the non-linear chemical and physical processes which actually occur within the urban area, because these processes can cause results which are lower than, higher than, or differently distributed in the horizontal, vertical, or temporal domains, compared with the large-scale averaging or dilution approach. Urban scale processing causes certain species to have a positive net production (chemical production minus chemical, physical, and depositional loss) due to the inclusion of urban-scale processing. Three examples are CO (where production from VOC oxidation far outweighs loss due to reaction with OH), NO₂ (from photochemical processing), and certain lower molecular weight VOCs (from the oxidation of larger molecular weight VOCs). Other species are formed nearly exclusively in urban areas as secondary products, and involve significant non-linear processing, such as peroxyacetyl nitrate (PAN), secondary organic carbon aerosol (OC), nitrate aerosol (NO₃), and sulfate aerosol (SO₄). For all of these species, the dilution approach will not accurately simulate their concentrations in the urban area and their fluxes from the urban area to the global system. Other species have a negative net production due to processing in urban areas, such as some large VOCs (oxidized to smaller VOCs), NO, SO₂ (oxidized to NO₂ and SO₄), highly water soluble species (entering into the aqueous phase), and primary aerosols (removed through coagulation, rain out, and deposition). For these species the simple dilution approach will also erroneously calculate their concentrations in the urban area and their flux from the urban area to the global system. A third subset of species can have either a positive or negative net production, such as: O₃, OH, some VOCs, and some optically important aerosols. This subset of species has behavior that depends on many factors, such as the concentrations of other species in the urban area, whether it is raining or dry, the strength of vertical advection and mixing, and the time of the day. In the case of these species, the simple dilution approach can potentially either underestimate or overestimate the concentration in the urban area and the flux from the urban area to the global system.

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Furthermore, the simple dilution approach does not capture the vertical, horizontal, and temporal characteristics of the urban concentrations or the fluxes from the urban region. For example, modeling the processing occurring due to a small region of strong uplift, subsidence, or rainfall, over a heterogeneously distributed concentration field, can yield substantially different results than predicted by the simple averaging occurring in the dilution approach (which includes averaging the effects of the vertical air motion or the rainfall). This short-coming has been demonstrated in a study using ozone as an example, in which incremental improvements in the spatial resolution of the models emissions, chemistry and physics made the results compare more closely with measurements (Wild and Prather, 2006). However, even such efforts have only looked on horizontal spatial scales on the order of a degree, which are still far too coarse to precisely model processes occurring on the urban scale.

In this paper, we will describe the production of a metamodel (or a model of a model) which can simulate urban scale processing. The metamodel is computationally fast and capable of interacting in a two-way fashion as a component in a larger global-scale modeling system. The metamodel reproduces fairly accurately the underlying parent model simulations of the urban concentrations, deposition fluxes, and lateral and vertical mass fluxes to the global scale, under typical present day and potential future conditions. Sensitivity tests and comparisons of the parent model and with observations from different urban areas reveal that the metamodel is quite successful in simulating the species of interest.

2 Prior reduced form urban process models

An early attempt at forming a parameterization of urban scale processing was made by Calbo et al. (1998). They used the California Institute of Technology urban model, driven by idealized (non-divergent, single directional, non-evolving) meteorology, and a simplified version of fast NO_x and VOC photochemistry which in turn drove ozone production for their gas-phase chemistry driver. The model was run using five layers

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in the vertical, with initial conditions being zero for many species outside the bottom two layers. The latitudes for which this reduced form model was developed included the regions from 60° S to 60° N latitude. The average surface temperature and mixed layer height were scaled by a predefined function over time of the day. The fractional cloud cover was constant in both space and time. The residence time of an air parcel in the urban area was determined from the wind speed across the urban box model, and was constant over time. All emissions were assumed to occur within fixed geographical regions of the urban box model (near the center), at the same fixed ratios to one another, and as a fixed function of distance from the center of the urban area. The emissions of VOC and NO_x were defined in such a way as to be correlated with the emissions of CO, not allowing for conditions in which there was a strong reduction in just one or two of these three species. Furthermore, the PDFs of the emissions of the input species were defined by beta distributions, and therefore had zero chance of being outside of the defined upper and lower boundaries. Finally, the initial conditions and boundary conditions were given using air quality indexes, which are defined based upon generally clean upwind conditions.

The authors produced their parameterization by using the probabilistic collocation method (PCM) (Tatang et al., 1997), which is a method by which their model's response space was approximated by a set of orthonormal chaos polynomials, which had their polynomial coefficients computed based on sampling the PDFs of the input variables. All of their input parameters were fit using second order polynomials for each of the 14 input variables, which included all first order, second order, and cross combinations of the input variables. Using this method, they showed that there was a reasonable fit between the metamodel and the parent model for the mass fluxes of gas-phase species from the urban area (the parameterized model being within a few to 40% of the parent modeled variable). The major exception was ozone.

A second attempt at an urban process PCM-based parameterization was made by Mayer et al. (2000), using the same parent model, chemical routines, and approach to idealized meteorology, as in Calbo et al. (1998). Some of the important differences

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between these two approaches are described below. All five layers in the vertical were initialized with non-zero initial conditions, the urban area was 200 km × 200 km, the emissions only occurred in a core area of about 150 km × 150 km, and the air entering was assumed to be clean, exclusively matching values found in remote locations. One further difference is that Mayer et al. (2000) treated the upwind concentration of NO_x as two separate input variables, one for the upwind concentration of NO and the other for the upwind concentration of NO₂. A third difference came from the variation of emissions as a function of time, with no diurnal variation of SO₂ emissions, and a constant and identical diurnal variation assumed for all other emitted gasses.

The most significant differences, however, came from how the uncertainties were treated. The emission PDFs were based on fits to a normal function, and therefore they had a non-zero probability of being any finite positive value. Furthermore, the emission PDFs were formed independently of each other, allowing for higher or lower values of each emitted species to be modeled, with all emissions values spread further than the beta PDF case, but still tightly concentrated around their median values. This change allowed for more regions of the parameter space to be explored by the metamodel. Finally, the probabilistic collocation method employed in this case used some selected third order terms in addition to the complete set of second order terms in their polynomial chaos expansion. These additional terms were added specifically to look at higher order effects on the net flux of ozone from the urban region. In general, the results from this effort showed a more reasonable fit than Calbo et al. (1998) for all mass fluxes of gas species of interest from the urban area, including ozone.

3 Parent urban chemical transport model

Regional scale models of atmospheric chemistry and physics can effectively simulate the processing of emissions on spatial and temporal time scales resembling those on the urban scale, allowing for both the time varying concentrations within and the time varying export from a specific urban area to be computed. The model chosen

to perform these calculations is the Comprehensive Air Quality Model with extensions (CAMx) (www.camx.com), which is an Eulerian model that solves the terrain following continuity equation, for the concentrations and fluxes of trace species. CAMx accounts for the emissions, vertical and horizontal transport and diffusion, gas and aerosol phase chemistry, and the wet and dry deposition of trace species. Additionally, CAMx takes into consideration how the properties of the Earth's surface, the given atmospheric conditions, and the amount of incident solar radiation as a function of space and time, further affect the concentrations and distributions of trace species. Much of the recent peer-reviewed literature relating to urban and regional air quality has relied on CAMx (see, e.g., Russell and Allen, 2005).

The specific way in which CAMx accounts for these processes is by solving for each of the terms separately in Eq. (1):

$$\frac{\partial c}{\partial t} = -\nabla(cv) + \frac{\partial(c\eta)}{\partial z} + c \frac{\partial}{\partial z} \frac{\partial h}{\partial t} + \nabla \left(\rho K_v \nabla \frac{c}{\rho} \right) + \frac{dc}{dt} \Big|_{\text{chemistry}} - \frac{dc}{dt} \Big|_{\text{deposition}} - \frac{dc}{dt} \Big|_{\text{removal}} \quad (1)$$

In this equation c is the concentration (moles or mass per unit volume) of a given species, v is the horizontal wind velocity, η is the vertical wind velocity, h is the vertical layer height, ρ is the atmospheric density, and K_v is the turbulent exchange diffusion coefficient. The equation states that the net change in the concentration of a given species is the sum of: the convergence of the advective flux in the horizontal and vertical, and the diffusive flux; the chemical production and destruction, emissions, wet and dry deposition at the surface, and other physical removal processes (such as capture by cloud particles).

However, solving this equation is neither straight forward nor simple, requiring many assumptions. Firstly, all processes are treated as though they are uniformly distributed through each Eulerian grid box in which they occur; therefore emissions are diluted through the grids adjacent to the surface, physical and meteorological variables are assumed to have a single average value over a grid box, and tracers are considered to have a constant concentration throughout a grid box. The advection routine is solved in mass-conserving flux form, driven by realistic assimilated meteorology from the 1995

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OTAG (<http://capita.wustl.edu/otag/>) campaign at four different sites, all using data from the same 2-day period of data collection (Vukovich, 1997). The amount of liquid water in the form of rain, the amount of cloud cover, and the mass flux of air (integrated over all four sides and the top of the urban area) through the boundaries of the urban area, are given in Table 1. These meteorological conditions were chosen to cover typical ranges for rainfall, cloud cover, and the net mass flux of air integrated across all five boundaries of the urban area. In this way, some extreme conditions which are likely to be found in generalized urban areas can be simulated, with less extreme conditions lying somewhere in between.

The vertical velocity is computed by integrating the density conservation equation. Wet removal occurs through Henry's Law processes, physical mixing, aqueous phase chemistry, and impaction by precipitation. Dry removal occurs through first order surface resistance removal schemes for gases and aerosols, and gravitational settling for aerosols. Gas phase chemistry is based on the Carbon Bond 4 approach (Gery et al., 1989; Sarwar et al., 2008), with a newer and more detailed representation of terpenes, low volatility organic species, and improved night time nitrogen chemistry. Aerosol phase chemistry includes explicit inorganic aqueous phase chemistry, inorganic thermodynamics, and formation of secondary organic and inorganic aerosol. This is performed over a size-based sectional scheme, using fixed values for the edges of the size bins. The photolysis scheme uses a lookup table based on the TUV model, and accounts for reducing fluxes of incoming solar radiation as a function of overhead cloud thickness and reflection, and for surface reflection. And finally, the precipitation processes include rain, snow, and ice (all of which are internally computed, based on the temperature and the strength of the vertical convection in the region).

4 Probabilistic collocation method

The computational expense of running a detailed urban model, such as CAMx, is very large. Thus, using such a modeling platform to directly model the effects of hundreds

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or thousands of different urban areas in the context of a global climate model is not computationally feasible. In addition to these direct computational expenses, there are further computational costs, such as two way interactions between the global model and the urban model relating to the physical and chemical variables which drive the temperature, rainfall, horizontal wind, and chemical concentrations at the boundaries between the two models. To form a computationally efficient parameterization of the processes contained in CAMx, we follow Calbo et al. (1998) and Mayer et al. (2000) and use the probabilistic collocation method (Tatang et al., 1997). This method is one of several mathematical techniques which can be used for creating a metamodel. Specifically, given a set of k input parameters x_j used to drive a model, $\{x_1, x_2, \dots, x_k\}$, there are M output responses y_j predicted by the model that are functions of the x_j values; $\{y_1, y_2, \dots, y_M\} = f(\{x_1, x_2, \dots, x_k\})$. In this case the y_j are the physical concentrations, mass fluxes, and deposition fluxes of species that we are interested in approximating. And since there is a range of possible values which each input parameter can take, each input variable is considered independent and has its statistics defined by its PDF over this range. Since all of the input variables are considered random, the output variables also are considered random variables.

The response surface is being fitted specifically by a set of recursively defined orthonormal polynomials (P_{k_i}) where i ($= l$ or m below) is the order of the polynomial, g is the PDF of the random input variable x_j , and δ_{lm} is the Kronecker delta:

$$\begin{aligned}
 P_{k_{-1}} &= 0 \\
 P_{k_0} &= 1 \\
 \int g(x_j) P_{k_l}(x_j) P_{k_m}(x_j) dx &= \delta_{lm}
 \end{aligned} \tag{2}$$

Through these polynomials (Eq. 2), the independent random variables can be written as $x_j = x_{j_0} + x_{j_1} \cdot P_{k_1}$, and the dependent variable y_j can be approximated by the

polynomial chaos expansion (Eq. 3):

$$y_j = y_{j_0} + \sum_{i=1}^N y_{j_i} P_{k_i} \quad (3)$$

where y_{j_i} is a coefficient to be fit based on the parent models predicted value for y_j at the given set of inputs $\{x_j\}$, and N is the order of the polynomial fit (in our case, full cubic).

In addition to forming the basis for the polynomial chaos expansion, the orthonormal polynomials are also used to help select the set of parameter values which are used to initialize the parent model. This set of input values, called collocation points, are solved for by finding the $N + 1$ roots of the $N + 1$ order polynomial corresponding to each input parameter x_j . These roots are from the high probability regions of each input parameter, and therefore the approximation of y_j is particularly good within the most probable range of values of the input parameters. In addition to this, a set of test points are generated from the solution of the $N + 2$ roots of the $N + 2$ order polynomial corresponding to each input parameter x_j . This second set of points form an excellent test for the metamodel in that they take into account what the next higher order of estimation would yield as a better set of points for sampling the probability space spanned by the input parameters.

5 Metamodel inputs and outputs

The smallest possible set of input variables capturing the effects of urban chemical and physical processing must be derived in order to form a reduced form model which is as compact as possible. This set of inputs needs to be flexible enough to be applicable to the many variations of the properties of urban areas found throughout the world both presently and in the future out to 2100. Specifically, the variables need to span the differences in geography, location, time of the year, atmospheric temperature,

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cloudiness, amount and type of precipitation, circulation, time tendency of emissions, spatial tendency of emissions, the amount of each type of emitted species, and the upwind concentrations of species of interest, as a function of space and time. Specifically, there are 18 uncertain input variables which are used to derive the model, each of which has its uncertainty based on a wide range of both present day conditions and those conditions expected out to 2100 (derived through the running of a set of climate policy and no climate policy economic scenarios using the MIT Joint Program's EPPA model (Paltsev et al., 2005)). These input variable PDFs are defined and described in Table 2 using the respective equations for Uniform PDFs 4 (where $a \leq x \leq b$), Beta PDFs 5 (where $a \leq x \leq b; p, q > 0$), and Lognormal PDFs (Eq. 6) (where $x, m, \sigma > 0$), where a, b, p, q, m , and σ are the parameters, and x is the input value.

$$f(x) = \frac{1}{(b-a)} \quad (4)$$

$$f(x) = \frac{(x-a)^{p-1}(b-x)^{q-1}}{(\int_0^1 t^{p-1}(1-t)^{q-1} dt)(b-a)^{p+q-1}} \quad (5)$$

$$f(x) = \frac{\exp\left(-\frac{[\ln \frac{x}{m}]^2}{2\sigma^2}\right)}{x\sigma\sqrt{2\pi}} \quad (6)$$

The first set of input variables in Table 2 are for the time, location, emission spatial distribution, and temperatures as discussed later. The second set of input variables are fluxes for those species that are directly emitted in the urban area. The directly emitted species are CO, NO_x (95% emitted as NO and 5% emitted as NO₂), VOCs, SO₂, BC (primary black carbon aerosol), and OC (primary organic carbon aerosol). The CO and BC emissions have been fitted by lognormal probability distribution functions, see Fig. 1, based on the results of 250 policy and 250 no policy runs of the MIT EPPA Model (Paltsev et al., 2005; Cossa, 2004).

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The remaining primary emitted species are chosen so that they linearly scale with the emissions of either CO or BC (these linear coefficients are listed in Table 2). One reason for doing this is that the sources of the gas-phase species CO, NO_x, and VOCs tend to be similar and those of the aerosol phase species and their precursors BC, OC, SO₂, and NH₃ also tend to be similar. Secondly, since the probabilistic collocation method samples the space best in regions which are of high probability, and since there is local correlation between these emissions they are not independent variables, a more reliable result is obtained using this method. The best fit linear relations between the emissions of these species are given in Table 5 using Eq. (7), where P is the emissions of the parent species in g day^{-1} , X is the emissions of the subordinate species in g day^{-1} , and β and α are the best fit coefficients for the slope and intercept, respectively.

$$X = \beta P + \alpha \quad (7)$$

Furthermore, this technique employing only two independent emissions species, CO and BC, has been found to be superior to the technique employed by Mayer et al. (2000) in the case where the emissions of all or most primary emitted species are all elevated. The superiority results from the fact that when seven different partly dependent variables are simultaneously sampled from low probability portions of their PDFs, the metamodel's reliability is inferior to when only 2 variables are sampled from low probability portions of their PDFs.

The third set of input variables in Table 2 are the mole fractions of trace species along the boundaries (the four sides and the top) of the urban area that impact the chemical and physical processing inside the urban area. The trace species that will be considered in this analysis are CO, NO_x, O₃, VOCs (represented by isoprene), and SO₂. To compute the mole fractions of these species, the aforementioned set of 250 policy and no-policy runs emissions were used for all species, except for isoprene. These were then used to drive the MIT Integrated Global Systems Model (IGSM) (Sokolov et al., 2005) to simulate the global concentrations of the relevant species, from the time period between 2000 and 2100. The simulated concentrations of the relevant species were

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aggregated over time, in the vertical up to the top of the urban modeling domain, and across all relevant latitude bands. These aggregated results were then fitted by lognormal probability distribution functions using a least-squares method. Since isoprene is not simulated by the IGSM, concentration data was taken from present and past measurements (Houweling et al., 1998; Yokouchi, 1994). The results of the aggregated data along with the best fit PDFs are given in Fig. 1.

The main problems with using the results from multiple runs of the IGSM to produce these various PDFs are that the IGSM does not produce results that provide a full probabilistic sampling of polluted upwind air and the MIT IGSM does not predict certain species which could be important, such as specific VOC species. However, using the IGSM gives a better indication of how these species will change over time, and since all are fit with lognormal PDFs, values which are considerably larger are better sampled. One way to improve this upon this would be to consider incorporating boundary conditions of anthropogenic and natural aerosols, such as BC, OC, sulfate, nitrate, mineral dust, and sea salt.

As noted in Table 2 the first two of these variables are the day of the year and the latitude of the urban region. These are both needed for computing the ultraviolet radiative flux. The day of the year is assigned a uniform PDF from 1 to 365. A beta fit of the distribution of latitudes of each urban area has been made for each region, making the assumption that each urban area is of equal importance. The latitudinal PDF for each region is given in Fig. 2.

The atmospheric temperature in the urban area and its range are important variables for determining the rates of many chemical reactions, Henry's Law partitioning, gas/aerosol phase partitioning, the concentration of liquid water in the urban atmosphere, and the size and total amount of precipitation. For the purposes of determining their global distribution, historical temperature data (Jones et al., 1999) has been weighted by the latitudinal beta PDFs, given in Fig. 2, for each urban area, and the resulting data fitted by a beta function. The average temperature of each of the 13 urban model vertical layers is computed assuming a linear decline with height with a standard

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linear lapse rate of 6.5 K km^{-1} . The spatial and temporal deviations from these layer averages in the temperature of each grid box of the urban domain are taken from the meteorology chosen for that particular urban region. The average daily surface temperature and average daily diurnal surface temperature PDFs are given in Fig. 2.

The final physical inputs to consider are rainfall and cloudiness, both of which impact the radiative fluxes, the uptake of soluble gases, and the removal rate of aerosols. After extensive testing, it has been found that treating these inputs as separate variables using the PCM approach does not yield reasonable results, due to the extremely non-linear impact these variables have on the system. Therefore, separate metamodels were formed for each of the four meteorological conditions.

Another set of driving variables are designed to simulate the transportation and habitation choices people make that have an impact on the processing of species in urban regions. The first variable represents the temporal distribution of emissions. It is commonly found that emissions in urban areas have a time profile which is doubly peaked, with the peaks occurring around the times of the morning and evening rush hours. Furthermore, the middle of the day is found to have a plateau with a considerably higher amount of emissions than the nighttime plateau, as shown in Fig. 3. To account for this, an input variable wt is defined that is uniformly distributed from 0 to 1, and is the weight given to this double peak temporal emissions spectrum when it is linearly added to a time invariant emissions profile. Therefore, for any given value of wt the weights assigned to the double-peaked distribution is wt and the weight assigned to the time invariant emissions distribution is $1 - wt$ (Yang et al., 2005). A second input variable relates to the spatial distribution of emissions in the urban region. Such a distribution must consider that urban areas vary greatly in terms of their density of people, activity, and thus emissions. Since most emissions are related to the population in urban centers, the emissions of both CO and BC are considered to be spatially correlated. These spatial distributions are fitted by a 2-dimensional Gaussian function whose standard diameter has a uniform distribution ranging from the assumed minimum size of a present world megacity of 21.6 km (Shenzhen, China) to the assumed maximum size

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of a present world megacity of 93.2 km (New York City Metro Area, USA). Two examples are given in Fig. 4, clearly showing the impact of this variable on the distribution of emissions.

Another input is required to address whether VOC emissions consist of a larger fraction of light hydrocarbons, corresponding to a more developed economy, or whether they have a larger fraction of heavier hydrocarbons, corresponding to a developing economy. Developed countries are assumed to have their VOC speciation follow the IPCC Third Assessment Report guidelines for Developed Nations emissions speciation of VOCs, while the rest of the world follows the IPCC Third Assessment Report guidelines for Developing Nations emissions speciation of VOCs (Prather et al., 2001). Since this final decision determines whether there are zero or non-zero values of many VOCs, the metamodels are expected to produce different results in the developed and developing regions of the world.

As previously mentioned, the impacts of the circulation, water content, and temperature on the processing in urban areas must be considered in detail. To address this issue, four different realistic sets of meteorology have been used to drive the urban modeling system. The point of employing these widely different cases is to numerically analyze the impact of adopting different types of realistic meteorology. This also allows for the feedback of rainfall in the global scale parent model to influence the processing at the urban scale, by providing a way to apply the same amount of rainfall, in a non-uniform manner.

The specific outputs from CAMx which were fit include chemical mole fractions/concentrations of trace species in the urban area (ppm for gases and $\mu\text{g m}^{-3}$ for aerosols), the net mass flux of trace species through the boundaries of the urban area kg day^{-1} , the mass flux of trace species deposited to the surface kg day^{-1} , and the concentrations of 7 specific trace species, of interest to human health and policy, over the bottom three vertical layers of the urban area (under 100 m) (ppm for gases and $\mu\text{g m}^{-3}$ for aerosols). The simulated trace gases and aerosols were averaged over space and time to produce 24 h averaged concentrations and had their export fluxes, deposition

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fluxes, and chemical production terms integrated over space and time to produce 24 h total values for each of the the 17 output trace gases and 8 output aerosol species. The exception to 24 h averaging is for those species specific to specific human health input calculations, which have been averaged over the appropriate time span for each given species. The specific species simulated by the reduced form models are given in Table 3 for both the climate and human health related outputs.

The parameterizations formed in this work are based on a full third order polynomial chaos expansion, which also includes all third order cross terms, all degenerate second order terms and cross terms, and all degenerate first order terms, for all 18 input variables. The fits were performed using the probabilistic collocation technique. Since the majority of the predicted species have non-linear gas-phase, liquid phase, or heterogeneous chemical or physical processing, their concentrations on the urban scale are not accurately predictable using typical global model grid sizes. The non-linear processing, production, and transformation lifetimes are shorter than or similar to the timescales of large scale advection, mixing, and chemical processes found in typical global models. Therefore, the point of using a full third order expansion was to obtain a good fit to the highly non-linear processing.

The consideration of urban processing requires that the spatial and temporal resolution in the urban model be sufficiently fine so as to resolve these non-linear effects. To achieve this, the urban area was modeled using an Eulerian framework, with a uniform horizontal grid spacing of 4 km \times 4 km in the north/south and east/west directions, over a total region of 108 km \times 108 km. In the vertical, 13 layers were chosen with pressure coordinates, from the surface up to the free troposphere, as given in Table 4. CAMx was specifically integrated forward with the time step only allowed to vary between 1 min and 3 min, so that the numerical solution of the equations would always remain stable. Finally, to make sure that any initialization assumptions were not affecting the results, the urban model was integrated for 96 h, with the initial 72 h being treated as a spin up and the final 24 h being the result used.

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6 Differences between this work and previous work

A significant difference between our new approach and prior efforts is inclusion of the impacts of liquid water, and its associated chemical and physical processes which do not occur under the dry conditions in prior efforts. These effects include: aqueous chemistry, uptake of soluble gases from the gas to the aerosol phase (including sulfuric acid), and wet deposition.

Another significant difference is inclusion of regions of strong vertical advection. Although the CAMx domain only goes to 710 mb, the underlying meteorology fields are based on results computed throughout the troposphere and therefore already include the effects of convection. These regions allow for efficient transport of trace species through the boundary layer, thereby altering their rates of chemical and physical transformation, surface deposition, and hence their lifetimes within the urban area. These effects can be especially important for photolysis reactions, temperature dependent reactions, or for species having strong liquid water or aerosol uptake potential. These effects can substantially increase or decrease the amounts of species exported from an urban area.

A third significant difference comes from the consideration of temporal and spatial variability in both atmospheric properties and surface emissions. For example, changes in the height of the boundary layer affect the net transfer in the vertical of trace species, and whether these species are shielded from or exposed to sunlight. Furthermore, emissions occurring at different times of the day lead to a difference in the local concentrations near the surface. These properties lead to considerable changes in mass fluxes and to non-linear chemical feedbacks. By specifically addressing these processes, our current modeling effort is an improvement over our previous modeling efforts, which used non-varying, uniform, and non-divergent winds which flow only from west to east. A further improvement is the use of multiple cases of meteorology. This enables studies of the effects of differences in rain and wind fields within the urban region.

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There are some effects, however, which could not be included but could be important to address in the future. The inclusion of meteorology for regions which have complex topography (such as Mexico City or Chongqing) or for regions located in equatorial latitudes (such as Singapore), would further provide a more realistic treatment in these urban regions. Furthermore, inclusion of realistic meteorology as a function of different seasons of the year would also provide a more realistic treatment of urban processing with respect to annual cycles. Other improvements could include dynamical feedbacks such as: consideration of urban scale topography, online calculation of absorption and scattering, and urban hydrological processes.

The Probabilistic Collocation Method using third order fits is a significant improvement when compared with our previous efforts, which only used second order fits. In particular the following species have had their prediction capability improved, or were not modeled in previous efforts: primary aerosols, secondary aerosols, aerosol precursors, aerosol size distributions, ozone, PAN, and certain VOCs. An additional benefit derives from the fact that using a higher order polynomial fit requires that more specific points be sampled from each input PDF. Hence the metamodel is more precise for more extreme values of the input, while still allowing for the polynomial fit to be more reliable near the center of the input PDFs. As discussed later, this improvement was demonstrated by using the input variables that would be used to build a full fourth order polynomial approximation to test the third order metamodel's performance.

7 Concentrations, mass fluxes, and deposition

For the parent CAMx model runs, we have examined the results for the urban concentrations, mass fluxes from the urban area, and mass fluxes deposited to the surface in the urban area, for each trace species. When looking at the results of the concentrations in mole fraction form, regions of different mole fractions must have a change in chemical production (production minus loss) of the species. Furthermore, for a species to have a mass flux which is not equal to its emissions, there must be a net amount of

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chemical processing, deposition, or convergence or divergence in the continuity equation (Eq. 1). A convenient metric is the ratio of the mass exported from the urban areas, to the mass emitted into the urban areas:

$$\frac{\text{Flux}}{\text{Emiss}} = \frac{(\text{Emiss} + \text{Chem} - \text{Dep})}{\text{Emiss}} = 1 + \frac{\text{Chem}}{\text{Emiss}} - \frac{\text{Dep}}{\text{Emiss}} \quad (8)$$

Here the Flux is the net mass flowing out through the 5 boundaries of the urban region g day^{-1} , accounting for the total budget within the urban area; Emiss is the net mass flowing into the urban area at the surface g day^{-1} ; Chem is the net mass undergoing chemical production or destruction within the urban region g day^{-1} ; and Dep is the net mass deposited to the surface of the urban region g day^{-1} . Using this metric, if the flux term is positive and larger than the emissions, then the in-situ chemical net production must be larger than the in-situ losses due to deposition. Conversely, if a species has a flux term which is positive but smaller than its emissions, its losses due to deposition must be greater than its net chemical production. Furthermore, for a species to have a negative flux term, then it must have an in-situ net chemical loss large enough to consume not only all of the mass emitted at the surface, but also some of the mass transported through the boundaries into the urban area.

This mass flux to emissions ratio therefore provides two efficient ways to test the validity of the model results (see Sect. 8). Firstly, any species which has a clean (zero) upwind boundary condition must have a flux to emissions ratio larger than or equal to zero. Secondly, a species which has no atmospheric chemical production sources in the urban area, such as Black Carbon, must have a flux to emissions ratio smaller than or equal to 1.0.

The essential test of the reliability of the reduced form model's precision and accuracy is to see how its outputs compare with the parent model. This was determined by analyzing the concentrations, mass fluxes, and surface deposition computed from running the parent model and the metamodels at all of the third and fourth order collocation points. While this test does not determine the accuracy and precision of the underlying CAMx model, we emphasize that testing of CAMx has already been

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carried out by many others (see Sect. 3). Scatter plots of these results, with the parent model value on the x -axis, the metamodel value on the y -axis, the ideal fit line (parent model = metamodel), and the associated RMS error, are given for BC mass, OC mass, sulfate mass, ozone, CO, formaldehyde, NO_2 , and PAN) for each of the metamodels is given in the supplemental material. The RMS and normalized RMS errors are computed using Eqs. (9) and (10), given that X_i is the value computed by the metamodel, X_{i^*} is the value computed by the CAMx model, and n is the number of points analyzed.

$$\text{normalized RMS} = \frac{\sqrt{\sum_{i=1}^n \frac{(X_{i^*} - X_i)^2}{n}}}{\sqrt{\sum_{i=1}^n \frac{X_i^2}{n}}} \quad (9)$$

$$\text{RMS} = \sqrt{\sum_{i=1}^n \frac{(X_{i^*} - X_i)^2}{n}} \quad (10)$$

The RMS error associated with the third order data points is representative of how well the metamodel corresponds to the data that was used to fit it. The error associated with the aggregated set of third and fourth order data points is representative of how well the metamodel performs when used under realistic modeling conditions, at which the inputs are constrained only by their input PDFs. The results are given, for the same species as above, in Tables 7 and 8 for the aggregated set of third and fourth order data points.

The first conclusion is that the parent and metamodel outputs when analyzing only the the third order input points, fit almost perfectly. A second conclusion is that there are a small number of outliers generated by the metamodel when the model is tested using the fourth order input points, under some model and meteorological conditions. It is these few significant outliers which contribute to almost all of the RMS differences

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from the ideal fit. All of these outlying points are due to having at least one input which is outside of the space spanned by the third order collocation points. This is not an unexpected result.

The results of the statistical analysis of the third order collocation points are nearly perfectly consistent for the concentrations, mass fluxes, and deposition fluxes of all species, under all of meteorological conditions, using all of the metamodells. The value of the normalized RMS error is always less than 1.8×10^{-5} for the China metamodel, 1.6×10^{-5} for the India metamodel, 1.6×10^{-4} for the developed metamodel, and 4.5×10^{-5} for the developing metamodel. This shows that the metamodells behave precisely and accurately, in relation to the parent model, at input values close to the third order collocation points. Furthermore, since the input values are based on data which is significant to only two or three decimal places, the errors are smaller than the significance levels of the input parameters, and are therefore effectively close to perfect.

The results of the analysis of the RMS errors of the concatenation of the third and fourth order collocation points is always less than 10% under all meteorological conditions, for all metamodells, and for all quantities being modeled for ozone, CO, NO, NO₂, H₂O₂, BC mass, and BC number.

Sulfur is not predicted as accurately, partially due to the multiple pathways by which sulfate aerosol is produced; the major pathway usually involves liquid water and some non-linear processing in the aqueous phase, but under cases with a heightened OH concentration, the usually slow gas-phase production mechanisms can become important. Generally the daytime OH concentration is between 1.0×10^7 molec cm⁻³ and 5.0×10^7 molec cm⁻³, which is 1 to 2 orders of magnitude larger than the concentrations found at the global scale. The maximum OH concentration can exceed 9.0×10^7 molec cm⁻³ under certain conditions. This is shown by the fact that sulfur is predicted reasonably well, except in the case of the developed city metamodel. This case has an overall lower OH concentration (on order of 20% to 50% less), yet a larger spread in the OH concentration between different input cases, with the maximum OH

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concentration levels similar to the maximum in the other cases. This difference in OH is likely due to two reasons: firstly, there are significant amounts of light VOCs emitted in the developed regions, and secondly, the developed regions have a very different ratio of NO_x to VOC emissions. Further compounding the issue is the fact that the meteorology case which is modeled the least well (R021-F19-W57) has the most extreme horizontal and temporal gradients of cloud cover and liquid water content. Under such conditions, the numerics of the model do not fare as well when looking at the contribution to an average net flux from an urban areas, or average concentration within the urban area. However, the normalized RMS errors for SO_2 , sulfate aerosol mass, and sulfate aerosol number, are always less than 10% for all quantities being modeled, except for the developed metamodel, meteorological scenario R021-F19-W57, where the normalized RMS error for SO_2 is less than 15%, and the normalized RMS error for sulfate aerosol number is less than 11%.

VOCs and OC are less well predicted than the other gas phase species and BC. Part of the reason is due to the variation in the OH fields. However, the different VOC emissions profiles have a further impact, since some species have negligible emissions in the developed city metamodel cases. The resulting concentrations are so small that the fits are neither precise or relevant to the net fluxes from the urban area. Specifically, the normalized RMS errors for formaldehyde, acetaldehyde, toluene, xylene, ethene, ethane, OC mass and OC number are always less than 10% except for the developed metamodel. The normalized RMS errors for formaldehyde and acetaldehyde are always less than 10%, except for the deposition value in the R021-F19-W57 meteorological case, where they are less than 24% and 14%, respectively. The normalized RMS errors for toluene and xylene are always less than 10%, except for meteorological case R021-F19-W57, where they are always less than 28%. The normalized RMS errors for ethene and ethane for the developed metamodel are unacceptably large except for meteorology cases R002-F02-W16 (errors always less than 10%) and R000-F00-W44 (errors always less than 29%). This is because these two cases have longer air residence times in the urban area, less variation in rain, and less variation in

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solar insolation, and so there is more chance for the chemical processing to come to something closer to a pseudo-steady state. Finally, due to the fact that some of the OC production is based on secondary processing of heavy VOCs, the normalized RMS error for OC is not as good as that of BC for the developed city metamodel. However, only in scenario R021-F19-W57 is the normalized RMS error greater than 10%, although it is still less than 20%. This is because in the high rain scenario, the effect of wet deposition dominates while in the low rain scenarios, secondary chemical processing is what dominates.

Ammonia is well predicted, except for the case of the developed city metamodel. Here the deposition of ammonia is imprecise because the amount of ammonia deposited is extremely small compared with the amount emitted and chemically processed. In this case, the majority of ammonia is converted into aerosol. However, since deposition accounts for only a very small amount of the loss of ammonia from the urban environment, the concentration and mass fluxes are both always modeled with a normalized RMS error of less than 10%.

Finally, PAN is reasonably well modeled except in the developed city metamodel. This logically follows from the above analysis and the fact that PAN is based on the chemistry of both the nitrogen (NO_2) and VOC (peroxy acetyl radicals) cycles. The deposition of PAN is found to have a normalized RMS error of less than 28%, the mass flux is found to have a normalized RMS error of less than 13%, and the normalized RMS error of the concentration is always less than 10%.

These results demonstrate that the meteorology plays a significant role for many species. In rainy meteorological conditions, much of the chemistry is dominated by the aqueous phase and wet removal. In dry meteorological conditions, the results are influenced by greater UV, different amounts of vertical advection, limited wet removal, and considerable dry aerosol processing. In addition, meteorological scenarios which are more variable tend to produce large spatial and temporal gradients, causing net urban variables to behave less linearly. Finally, the time scale over which the species remain in the urban area is very important, with the processing likely to be more complete, and

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hence easier to predict, the longer the residence time of air in the urban area.

8 Sensitivity and observational tests

The sensitivity of the response of these metamodels to different input parameters has been investigated, to determine their reliability and efficacy under many different input conditions. The results from the polynomial fits should be robust under input conditions which are in the high probability region of their distribution, based on the type of urban regions, and changes in time. To accomplish this investigation, each metamodel was run using the same set of 50 000 independently and randomly sampled numbers chosen by selecting a random number between 0.15 and 0.85 for each input variable. This number was then used as the CDF (cumulative distribution function), thus defining a choice for the input variable. PDFs of each of the input variables so generated, for each of the different metamodels, are given in Fig. 5. This process enables testing of the metamodels at input values that evenly favor both the highly probable and less probable regions of the input variables.

A further test of the efficacy of the metamodels sensitivity is to compare the results with measured urban mole fractions and concentrations. Although these are not exactly the same thing, since the measured values from urban areas are usually point measurements taken near the surface, the orders of magnitude should at least be comparable. For species with a large surface source, it is expected to have a modeled volume-averaged value lower than the actual measured values, and conversely in the case of species with high destruction near the surface.

Six of the species that are important both on the urban and global scale, and have measurements readily available in urban areas are ozone, CO, formaldehyde, BC, OC, and sulfate, the latter three contributing to the total urban particulate mass concentration. The results for each of these species is shown in parts of Figs. 6, 8, 10, and 12, respectively for the China, India, developed, and developing metamodels, where the results of the 50 000 runs are compared with the minima, medians, means, and maxima

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for the measurements on the same plots. In general, the results of this sensitivity analysis compare reasonably well with the actual measured mole fractions and concentrations of ozone, CO, formaldehyde and BC in each simulated area.

The maximum ozone concentrations predicted by the metamodel are slightly higher than observed for the maximums, while the medians predicted by the metamodel compare reasonably well with measured median concentrations. The ranges of the maximum and median concentrations are given in Table 6. These metamodel medians and maxima are larger than the observed mean monthly average value of 23 ppb and maximum monthly average of 110 ppb found in the Guadalajara, Mexico urban area (Ramirez et al., 2009). As expected, the model results are higher than the measured values, because the model is giving the total vertically averaged ozone concentration in the urban area, which includes the upper regions which have no surface deposition, less titration by fresh NO emissions, and further time for the NO₂/NO ratio to increase.

The order of magnitude of the CO concentrations predicted by the metamodel is reasonable, with the ranges of the maximum and median concentrations also given in Table 6. These results are somewhat lower than the average observed monthly average concentration of 1.9 ppm and the observed maximum monthly average concentration of 9.2 ppm found in the Guadalajara urban area (Ramirez et al., 2009). As expected, the modeled values are slightly lower than the measured values, since the background CO concentration is usually lower than the surface CO concentration due to surface emissions.

The formaldehyde concentration predicted by the metamodel shows ranges of the maximum and median concentrations that are given in Table 6. The metamodel results are low or comparable to a) the observed average monthly concentration of 4–9 ppb and observed maximum average monthly concentration of up to 35 ppb in Mexico City (Lei et al., 2009), and b) the observed mean daily values of 10–19 ppb and maximum daily value of 46 ppb for Kolkata India (Dutta et al., 2009). The modeled concentrations are expected to be lower than the surface measurements, both because the background formaldehyde in the parent model run is zero, and surface emissions enhance

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the surface concentrations.

The ranges of the maxima and medians of the BC mass concentration, as predicted by the metamodells are shown in Table 6. These values are generally lower than the August 2006 average BC concentration in Hyderabad, India of $12 \mu\text{g m}^{-3}$ (Badarinath et al., 2009); a March to May monthly average high and low concentration of BC in Hyderabad of $5\text{--}35 \mu\text{g m}^{-3}$ and in Delhi, India of $5\text{--}45 \mu\text{g m}^{-3}$ (Beegum et al., 2009); a November 2006 to February 2007 monthly average BC concentration in Karachi, Pakistan of $10 \mu\text{g m}^{-3}$, a June to September monthly average Karachi BC concentration of $2 \mu\text{g m}^{-3}$, and a daily mean Karachi BC concentration in the range from $1\text{--}15 \mu\text{g m}^{-3}$ (Dutkiewicz et al., 2009); a Lahore, Pakistan average Winter BC concentration of $21.7 \mu\text{g m}^{-3}$, with the range over any given day from $5\text{--}110 \mu\text{g m}^{-3}$ (Husain et al., 2007); and a Rio de Janeiro mean annual BC concentration of $1.4\text{--}3.3 \mu\text{g m}^{-3}$ (Godoy et al., 2009). Since the background boundary concentration of BC in the model is assumed to be zero, and since the maximum concentrations are near the surface source, the average BC concentration in the model should be lower than the measured values.

The ranges of the maxima and medians of the OC and sulfate mass concentration, as predicted by the metamodells for each meteorological scenario are further shown in Table 6. Adding the mass concentrations of BC, OC, and sulfate provide the total anthropogenic component of the PM value as provided by the metamodel. Although this is not the equivalent to PM, since it does not include anthropogenic nitrate aerosol, or non-anthropogenic aerosols such as dust, sea salt, and forest fire aerosols, it can provide a lower bound estimation, particularly in areas which do not have large natural upwind sources of aerosols. These metamodel values are lower than the observed total PM_{10} monthly average concentration of $51 \mu\text{g m}^{-3}$ and a maximum monthly average concentration of $265 \mu\text{g m}^{-3}$ found in the Guadalajara urban area (Ramirez et al., 2009).

Furthermore, the flux to emissions ratio for each of these species has been investigated and compared with the ratios expected to result from the chemical and physical

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processing of the species. The graphs of these ratios are given in Fig. 7 for the China metamodel, Fig. 9 for the India metamodel, Fig. 11 for the developed metamodel, and Fig. 13 for the developing metamodel, for BC, OC, sulfate aerosol, CO, NO₂, and formaldehyde. The median value of the ratio in the case of CO is close to 1.0 in all metamodel cases, indicating that the effects of deposition and chemistry are not significant when compared with emissions, over the 24 h timescale of the urban metamodel run. This means that a significant fraction of the VOC may not be fully oxidized to CO by the time it has been exported from the urban area, since the deposition of CO is negligible.

The flux to emissions ratio for formaldehyde can be used to investigate the extent of the VOC emissions oxidized before being exported from the urban area. In the case of formaldehyde there are a few competing factors. First, in cases of large rainfall or cloudiness, less formaldehyde is produced through photochemistry and more is removed through wet deposition. In these cases, the median value of the ratio is found to be small, often under 0.2, whereas in cases of little or no rainfall and thin or no cloud cover, the median of the ratio, is up around 0.4. Second, in the cases of low molecular weight VOC emissions typical in developed urban regions, the median value of the ratio can be as high as 0.8 depending on the meteorology, due to the more rapid oxidation of light VOCs into formaldehyde.

The flux to emissions ratio for NO₂ is useful for determining what the expected ozone production will be downwind from the urban area. Since only 5% of the emissions of NO_x is in the form of NO₂, any ratio which is larger than 0.05 indicates an increase in the export of NO₂, with respect to the simple dilution approach. The results show that the median value of the ratio actually ranges from 0.1 to 0.4, depending on the meteorology scenario.

The flux to emissions ratio for BC should be and always is in the range from 0.0 to 1.0. It is also a very strong function of the amount of rainfall, with the median value being as low as 0.35 in the case of high rainfall and the median value being as high as 0.95 in the case of no rainfall. This further indicates that dry deposition is much less

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important than wet deposition in the case of BC.

The flux to emissions ratio for OC should always be the same as or larger than BC, since the sources of OC are emissions, which are correlated linearly to those of BC, plus a small amount of secondary production due to oxidation and condensation of high molecular weight VOCs. This results in the median ratio of OC always being about equal to that of BC in the cases of high rainfall (in which case these low vapor pressure secondary products are also more efficiently removed, and less efficiently oxidized due to a lessened actinic flux), and from 1% to 5% higher in the case of low rainfall.

Finally, the flux to emissions ratio for SO₂ should always be larger than or equal to 0.0, indicating how much of the gas is converted to sulfate aerosol as a result of urban processing. The ratio is a less strong function of the rainfall for SO₂ than for BC and OC. This results from the fact that an important production mechanism for sulfate aerosol requires the presence of liquid water (although the same removal mechanisms are at play for all three aerosol types). What is particularly interesting is that the median of the SO₂ ratio in the case of the India metamodel is from 0.05 to 0.10 larger than in the other three metamodel cases, for each of the meteorological scenarios. This is caused at least in part by the higher average temperature in Indian cities increasing the oxidation efficiency of SO₂ in both the gas and aqueous phases.

9 Conclusions

We have developed and tested a computationally efficient metamodel approach for analyzing the impact of the non-linear physical and chemical processing of the emissions of gases and aerosols in urban regions worldwide, which can be incorporated into a global chemical model. Since the majority trace gas and aerosol emissions occur in hundreds of urban centers, and since the effects of their processing have both local and global impacts on the direct and indirect radiative forcing of the climate, this is an important problem to address. Our reduced form metamodels have been formed to simulate these effects for urban areas in diverse geographical regions, for multiple

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realistic meteorological conditions, and for a range of human-induced patterns and distributions of anthropogenic emissions. These metamodels are specifically designed to efficiently simulate the urban concentration, surface deposition, chemical production, and net mass flux of species important to human health and climate.

5 These metamodels have been designed to be fast enough, so that they can be integrated into a global scale modeling platform and thus better capture the concentrations and mass fluxes found in real urban areas, as compared with the process of dilution of urban emissions into much larger grid volumes than the large-scale models currently use. Polynomial chaos expansions have been used to create and fit these metamodels
10 based on a broad range of conditions, applicable both to the present and hypothetical future world, so that they remain applicable both for current conditions and for studies which look at the chemistry of urban areas in the future. The various outputs are based on a set of 18 inputs, which include physical properties, such as the local temperature, daily diurnal temperature range, the day of the year, and the geographic
15 location. Secondly, they include the anthropogenic properties of urban emissions, such as the temporal and spatial weighting of emissions, and the magnitude of emissions of many relevant anthropogenic species. Thirdly, the remaining inputs include the upwind (or background) concentrations of trace species, both anthropogenic and natural in nature, which have an impact on the processing in the urban area. These inputs
20 have been gathered from multiple sources, and used to generate a set of PDFs of their potential values in current and future urban areas. In the final application, these inputs will come from the global model grid boxes containing the urban area.

These PDFs were then used to create the chaos polynomials in a recursive process and to determine inputs at a set of thousands of collocation points at which to run the detailed parent chemical and physical model, CAMx. Another set of higher order
25 points were also generated from these input PDFs, which were used to test the fit to the parent CAMx model.

The deviations between the metamodel and the parent model were computed in terms of a normalized RMS error. Many important species, such as ozone, CO, NO_x,

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and BC were found to have a normalized RMS error less than 10% for all of the meta-models, under all meteorological conditions, with many of the species having a normalized RMS error less than 1%. Some of the other important species, such as VOCs, PAN, OC, and sulfate aerosol are usually fit well, except for a few meteorological cases in just one of the metamodel regions, in which they are fit less well. This is associated with the highly non-linear source and sink processes of these chemical species, and the geographic areas and meteorological scenarios of choice. The reason for the less good fit in each of these cases is largely explained in terms of the complexity of this physical, chemical, and meteorological processing.

A set of sensitivity and observational tests have been performed to compute the response and accuracy of the various metamodels to a very broad set of potential inputs different from those used to produce the fits. The point of this testing was to determine if the metamodel could accurately handle multiple inputs from low probability regions of the input PDFs, and this was generally determined to be the case. Furthermore, these results were compared with observations of ozone, CO, formaldehyde, BC, and PM₁₀ from a few urban areas where they were available. In most of the cases, the output distributions were found to be similar to the observations, especially given that the metamodel predicts average urban concentrations, and not point surface measurements for these species.

It appears that these metamodels can efficiently and robustly simulate the urban concentrations, mole fractions, and fluxes of species, important to human health and the global scale climate. Hopefully, further investigations in this general area could lead to improvements of our understanding of the emissions of gasses, aerosols, and their precursors; the processing of aerosols at both large and urban grid scales; the modeling of non-linear effects that occur on scales smaller than the grid-scale; and the impact that sub-grid-scale urban processes have on the larger atmosphere.

Supplementary material related to this article is available online at:
[http://www.atmos-chem-phys-discuss.net/11/4631/2011/
acpd-11-4631-2011-supplement.pdf](http://www.atmos-chem-phys-discuss.net/11/4631/2011/acpd-11-4631-2011-supplement.pdf).

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- 30

Development of a fast, urban chemistry metamodelJ. B. Cohen and
R. G. Prinn**Table 1.** Physical descriptions of the four meteorological scenarios used to create the four metamodels.

Meteorology case	Rainfall (mg m^{-3})	Cloudiness (%)	Air flux (10^9 kg s^{-1})
R241-C63-W46	241.0	62.8	4.56
R000-F00-W44	0.00	0.00	4.38
R002-F02-W16	1.72	1.75	1.61
R021-F19-W57	21.5	19.3	5.70

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Table 2. Descriptions of and coefficients for the PDFs used to drive the CAMx model. The PDFs are defined based on Eqs. (4)–(6).

Variable	Type of PDF	China	India	Developed	Developing
Day of the year	Uniform (<i>a, b</i>)	1.000 365.0	1.000 365.0	1.000 365.0	1.000 365.0
Latitude of urban areas (°)	Beta (<i>p, q, a, b</i>)	3.663 3.897 22.7 44.3	1.736 1.694 9.70 31.4	5.802 9.842 34.7 51.3	3.309 2.625 -25.70 53.3
Temporal weight	Uniform (<i>a, b</i>)	0.000 1.000	0.000 1.000	0.000 1.000	0.000 1.000
Spatial weight (km)	Uniform (<i>a, b</i>)	21.6 93.2	21.6 93.2	21.6 93.2	21.6 93.2
Daily average surface temperature (K)	Beta (<i>p, q, a, b</i>)	3.924 1.583 251.9 303.3	8.483 2.810 267.4 309.4	7.827 3.446 261.7 310.7	2.637 2.006 263.2 301.8
Daily average diurnal temperature (K)	Beta (<i>p, q, a, b</i>)	3.841 4.125 3.061 15.06	1.741 1.976 5.318 18.76	4.114 3.368 2.073 16.45	2.532 3.438 4.037 21.24
CO emissions (ton day ⁻¹)	Lognormal (<i>m, σ</i>)	3162. 1.908	2398. 1.563	7171. 2.651	5713. 1.995
VOC emissions (ton day ⁻¹)	CO emissions ×	.0814	.2194	.2180	.1891
NO _x emissions (ton day ⁻¹)	CO emissions ×	.3558	.2462	.2815	.1721
BC emissions (ton day ⁻¹)	Lognormal (<i>m, σ</i>)	88.56 2.133	39.88 1.761	75.45 2.387	68.15 2.459
SO ₂ emissions (ton day ⁻¹)	BC emissions ×	.7646	.3526	1.966	1.481
NH ₃ emissions (ton day ⁻¹)	BC emissions ×	1.104	3.468	.9779	.6038
OC emissions (ton day ⁻¹)	BC emissions ×	1.615	1.586	2.587	3.890
Boundary ozone (ppb)	Lognormal (<i>m, σ</i>)	26.23 1.162	28.57 1.165	24.64 1.182	32.83 1.458
Boundary CO (ppb)	Lognormal (<i>m, σ</i>)	81.63 1.473	96.69 1.489	75.11 1.475	105.6 1.628
Boundary NO _x (ppt)	Lognormal (<i>m, σ</i>)	44.40 1.299	54.96 1.192	33.42 1.521	46.60 1.680
Boundary SO ₂ (ppt)	Lognormal (<i>m, σ</i>)	182.1 1.355	254.9 1.472	149.7 1.316	339.3 2.223
Boundary isoprene (ppt)	Lognormal (<i>m, σ</i>)	373.2 2.293	373.2 2.293	373.2 2.293	373.2 2.293

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Table 3. List of all species simulated by the urban metamodels. Unless otherwise stated as being a surface variable or having a specific temporal averaging, all species are simulated as a daily average value at each vertical level.

Ozone	Xylene	Black carbon mass
CO	C ₂ H ₄	Organic carbon mass
NO	C ₂ H ₆	Nitrate mass
NO ₂	Peroxyacetyl nitrate	Surface PM ₁₀
N _x O _y	H ₂ O ₂	Surface PM _{2.5}
HNO ₃	NH ₃	Surface 8 h ozone
SO ₂	Sulfate number	Surface 6 h ozone
H ₂ SO ₄	Black carbon number	Surface ozone
Formaldehyde	Organic carbon number	Surface NO _x
CH ₃ CHO	Nitrate number	Surface SO ₂
Toluene	Sulfate mass	

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Vertical Layer	Pressure (hPa)
1	990
2	980
3	970
4	960
5	950
6	940
7	930
8	910
9	890
10	860
11	830
12	780
13	710

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Table 5. Best fit emissions correlation statistics, based on Eq. (7). VOC and NO_x emissions are linearly related to CO emissions while OC, SO₂, and NH₃ emissions are linearly related to BC emissions.

Emitted species	Model location	Best fit slope β	Best fit intercept α
VOC	China	0.0814	0.0426
VOC	India	0.2194	-0.0190
VOC	Developed	0.2180	0.3250
VOC	Developing	0.1891	0.0571
NO _x	China	0.3558	-0.0933
NO _x	India	0.2462	-0.0711
NO _x	Developed	0.2815	0.4149
NO _x	Developing	0.1721	-0.0928
OC	China	1.6145	0.0063
OC	India	1.5864	0.0149
OC	Developed	2.5874	0.0044
OC	Developing	3.8897	-0.0179
SO ₂	China	0.7646	0.1138
SO ₂	India	1.3526	-0.0366
SO ₂	Developed	1.9656	0.1718
SO ₂	Developing	1.4809	0.1310
NH ₃	China	1.1041	0.0441
NH ₃	India	3.4816	0.0414
NH ₃	Developed	0.9779	0.0457
NH ₃	Developing	0.6038	0.0712

Table 6. Results of metamodel simulated urban area concentration medians and maxima, based on 50 000 randomly selected input parameters.

Species	Metamodel	Range of median values	Range of maximum values
Ozone (ppb)	China	88.4–113	326–418
Ozone (ppb)	India	118–154	311–436
Ozone (ppb)	Developed	58.4–84.3	293–1520
Ozone (ppb)	Developing	108–129	381–437
CO (ppm)	China	0.265–0.705	1.82–5.64
CO (ppm)	India	0.240–0.620	1.12–3.40
CO (ppm)	Developed	0.522–1.55	8.49–27.9
CO (ppm)	Developing	0.452–1.34	3.86–12.8
Formaldehyde (ppb)	China	0.332–1.73	6.82–18.1
Formaldehyde (ppb)	India	0.685–5.53	9.40–38.5
Formaldehyde (ppb)	Developed	0.746–107	23.5–250
Formaldehyde (ppb)	Developing	0.968–10.7	10.1–129
BC ($\mu\text{g m}^{-3}$)	China	2.60–20.1	27.8–208
BC ($\mu\text{g m}^{-3}$)	India	1.24–9.20	8.97–74.1
BC ($\mu\text{g m}^{-3}$)	Developed	2.19–16.3	29.6–229
BC ($\mu\text{g m}^{-3}$)	Developing	2.14–17.5	35.8–258
OC ($\mu\text{g m}^{-3}$)	China	4.22–32.8	45.2–337
OC ($\mu\text{g m}^{-3}$)	India	1.98–16.0	14.3–113
OC ($\mu\text{g m}^{-3}$)	Developed	5.75–28.8	77.0–4630
OC ($\mu\text{g m}^{-3}$)	Developing	8.53–73.6	140–1010
Sulfate ($\mu\text{g m}^{-3}$)	China	3.17–24.6	89.3–468
Sulfate ($\mu\text{g m}^{-3}$)	India	4.10–28.0	15.9–798
Sulfate ($\mu\text{g m}^{-3}$)	Developed	3.53–18.2	27.6–835
Sulfate ($\mu\text{g m}^{-3}$)	Developing	4.40–30.9	80.7–335

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Table 7. Normalized fractional RMS errors for species mole fractions/concentrations.

Species	China R241-F63-W46	China R000-F00-W44	China R021-F19-W57	China R002-F02-W16
BC mass	1.05E-02	1.31E-02	1.43E-02	3.05E-03
OC mass	1.05E-02	1.31E-02	1.43E-02	3.08E-03
Sulfate mass	5.23E-03	1.16E-03	1.43E-03	1.27E-02
Ozone	9.73E-05	1.23E-04	9.29E-05	3.90E-04
CO	1.06E-04	1.00E-04	1.15E-04	1.55E-04
Formaldehyde	3.77E-03	3.44E-03	2.95E-03	9.69E-03
NO ₂	9.20E-03	6.49E-03	1.04E-02	6.94E-03
PAN	1.85E-02	1.20E-02	1.39E-02	2.12E-02
Species	India R241-F63-W46	India R000-F00-W44	India R021-F19-W57	India R002-F02-W16
BC mass	1.24E-03	4.65E-03	7.42E-03	8.46E-03
OC mass	1.20E-03	4.69E-03	7.42E-03	7.98E-03
Sulfate mass	1.88E-03	6.74E-04	3.32E-03	2.66E-03
Ozone	1.73E-04	1.42E-04	1.69E-04	3.40E-04
CO	4.49E-05	4.41E-05	4.81E-05	6.53E-05
Formaldehyde	1.91E-03	1.44E-03	1.11E-03	4.18E-04
NO ₂	3.77E-04	3.47E-04	4.86E-04	5.10E-04
PAN	9.14E-03	3.92E-03	4.36E-03	1.07E-03
Species	Developed R241-F63-W46	Developed R000-F00-W44	Developed R021-F19-W57	Developed R002-F02-W16
BC mass	2.79E-02	3.56E-03	2.00E-02	3.02E-03
OC mass	2.74E-02	9.10E-02	1.62E-01	2.93E-03
Sulfate mass	1.08E-02	5.27E-02	8.59E-02	2.94E-02
Ozone	6.32E-04	7.09E-04	1.99E-03	1.03E-03
CO	5.86E-04	6.41E-04	1.28E-03	4.52E-04
Formaldehyde	7.12E-02	4.12E-02	1.77E-02	1.64E-02
NO ₂	2.48E-02	2.06E-02	2.36E-02	1.53E-02
PAN	9.08E-02	9.20E-02	4.31E-02	1.39E-02
Species	Developing R241-F63-W46	Developing R000-F00-W44	Developing R021-F19-W57	Developing R002-F02-W16
BC mass	1.33E-02	5.21E-03	2.27E-02	1.43E-03
OC mass	1.32E-02	5.03E-03	2.26E-02	1.37E-03
Sulfate mass	1.45E-02	1.85E-02	3.17E-02	2.47E-02
Ozone	1.87E-04	2.69E-04	2.51E-04	6.00E-04
CO	2.66E-04	2.90E-04	2.87E-04	3.74E-04
Formaldehyde	1.36E-03	3.57E-03	3.16E-03	3.26E-03
NO ₂	5.17E-03	6.60E-04	3.66E-03	1.90E-03
PAN	3.34E-03	1.90E-03	1.68E-03	4.09E-03

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Table 8. Normalized fractional RMS errors for species mass fluxes through the boundaries of the urban area.

Species	China R241-F63-W46	China R000-F00-W44	China R021-F19-W57	China R002-F02-W16
BC mass	1.03E-03	5.82E-04	4.34E-04	6.36E-04
OC mass	1.02E-03	6.16E-04	4.53E-04	6.80E-04
Sulfate mass	7.01E-03	3.80E-03	1.59E-03	4.72E-03
Ozone	7.38E-03	5.53E-03	5.95E-03	4.91E-03
CO	1.63E-04	1.69E-04	1.69E-04	1.94E-04
Formaldehyde	5.78E-03	3.60E-03	5.23E-03	9.42E-03
NO ₂	8.87E-03	5.83E-03	8.46E-03	6.39E-03
PAN	2.09E-02	1.27E-02	1.73E-02	2.07E-02
Species	India R241-F63-W46	India R000-F00-W44	India R021-F19-W57	India R002-F02-W16
BC mass	1.52E-04	1.82E-04	1.90E-04	1.60E-04
OC mass	1.40E-04	1.15E-04	1.30E-04	1.38E-04
Sulfate mass	5.61E-04	4.33E-04	3.41E-04	2.49E-04
Ozone	1.19E-03	1.11E-03	1.03E-03	1.07E-03
CO	1.15E-04	1.17E-04	1.22E-04	1.10E-04
Formaldehyde	2.77E-03	1.24E-03	2.09E-03	6.13E-04
NO ₂	4.47E-04	5.53E-04	4.38E-04	7.21E-04
PAN	1.06E-02	3.02E-03	5.87E-03	1.34E-03
Species	Developed R241-F63-W46	Developed R000-F00-W44	Developed R021-F19-W57	Developed R002-F02-W16
BC mass	1.47E-03	4.64E-04	2.38E-04	1.01E-03
OC mass	7.40E-03	7.47E-02	1.27E-01	6.26E-03
Sulfate mass	1.59E-02	8.20E-02	9.70E-02	2.20E-02
Ozone	1.99E-02	1.22E-02	3.56E-02	1.16E-02
CO	7.05E-04	8.53E-04	1.57E-03	5.15E-04
Formaldehyde	4.91E-02	3.90E-02	2.37E-01	1.45E-02
NO ₂	1.77E-02	1.16E-02	2.35E-02	1.21E-02
PAN	1.03E-01	9.26E-02	2.73E-01	1.83E-01
Species	Developing R241-F63-W46	Developing R000-F00-W44	Developing R021-F19-W57	Developing R002-F02-W16
BC mass	7.89E-04	7.50E-04	7.60E-04	1.40E-03
OC mass	7.78E-04	8.07E-04	8.02E-04	1.27E-03
Sulfate mass	6.64E-03	4.62E-03	9.83E-03	2.82E-02
Ozone	7.98E-03	6.39E-03	6.18E-03	6.00E-03
CO	6.35E-04	6.32E-04	6.35E-04	6.37E-04
Formaldehyde	1.06E-03	2.90E-03	1.82E-03	1.46E-03
NO ₂	1.37E-03	3.14E-03	1.53E-03	3.58E-03
PAN	3.35E-03	2.06E-03	2.60E-03	5.05E-03

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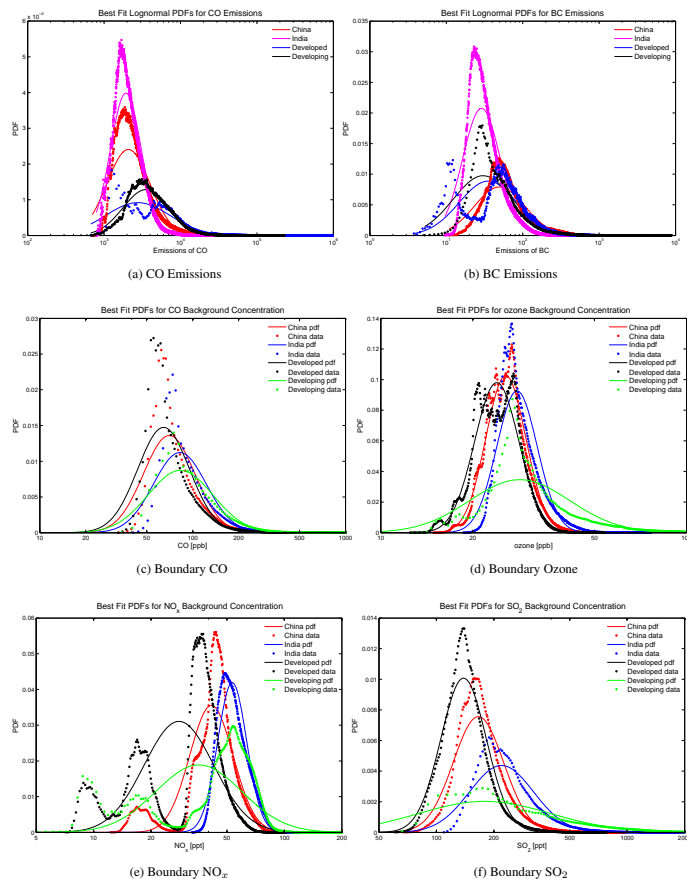


Fig. 1. PDFs of CO and BC emissions ton/day, and the boundary mole fractions of CO, ozone, NO_x , and SO_2 , for each metamodel type. The dots represent the aggregated, binned, and normalized data points, while the lines represent the best fit lognormal PDFs of the respective data sets. The coefficients for these best fit lognormal PDFs are given in Table 2.

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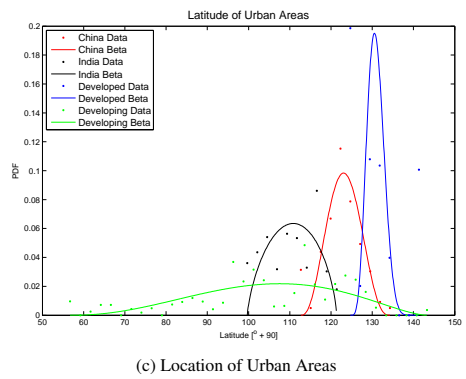
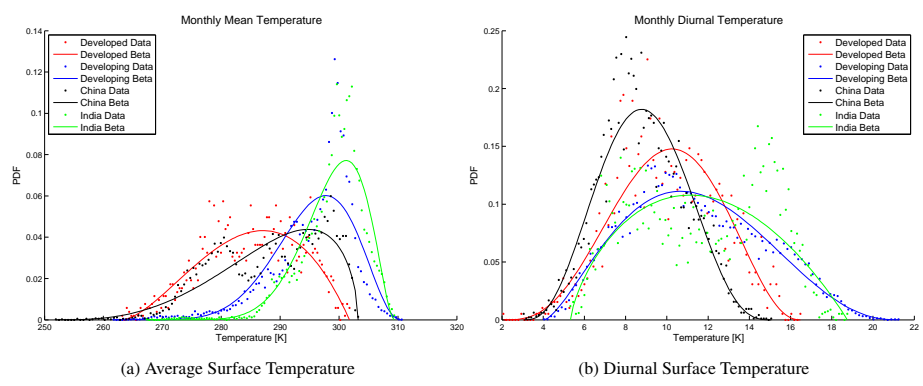


Fig. 2. PDFs of the number of degrees latitude north, from the South Pole, for the urban areas, where the dots are the fraction of urban areas in each latitude bin (urban area location data are from (for International Earth Science Information Network et al., 2000)); and the PDFs of the associated average daily surface temperature and the average daily diurnal temperature variation (daily high minus daily low) for each urban area, where the dots are the data for the monthly averaged respective values. In all cases, the lines represent the best beta function fits to the data.

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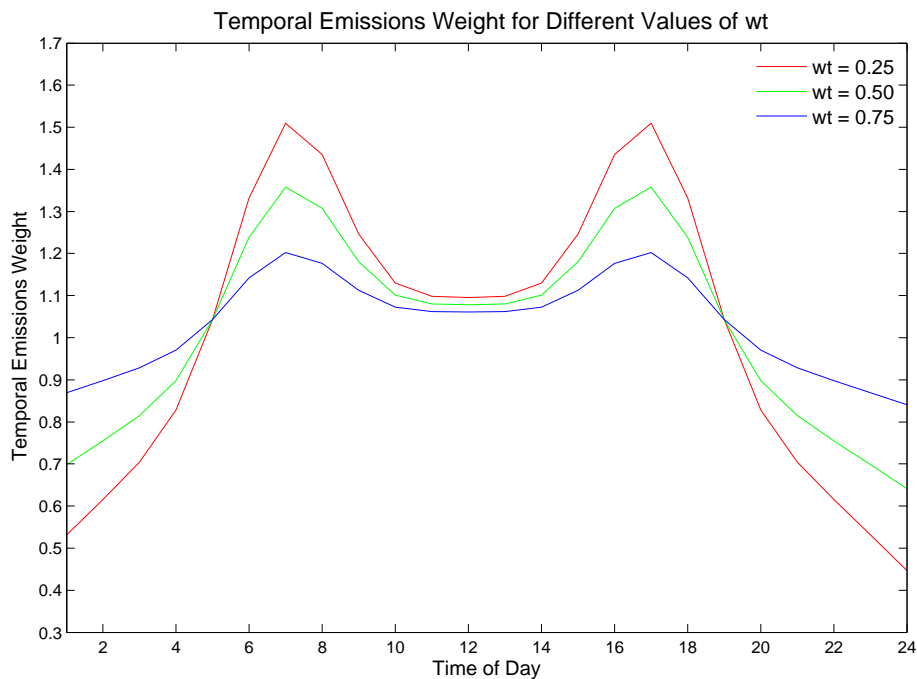
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Fig. 3. The temporal weight of emissions (normalized to unity), as a function of time, for an urban area. Specifically, this is the emission time distribution obtained for the input variable $wt = \{0.25, 0.50, 0.75\}$.

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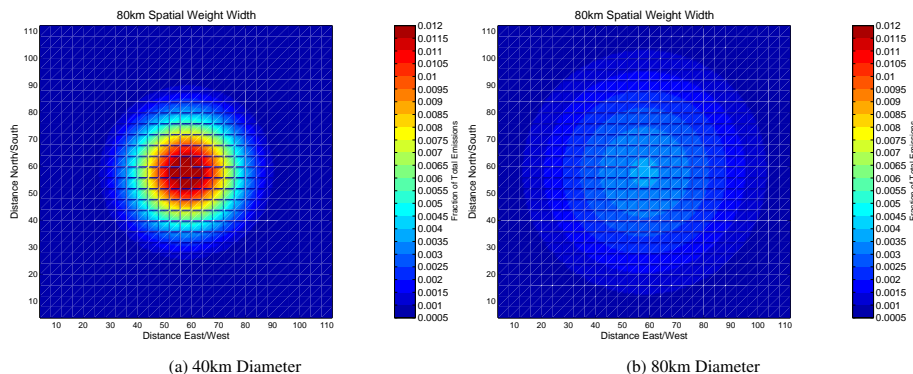


Fig. 4. Example of how the geospatial weighting of emissions impacts the distribution of urban emissions, for two example cases. Frame **(a)** corresponds to a gaussian standard diameter of 40 km and frame **(b)** to a gaussian standard diameter of 80 km. The color scale is identical for both plots.

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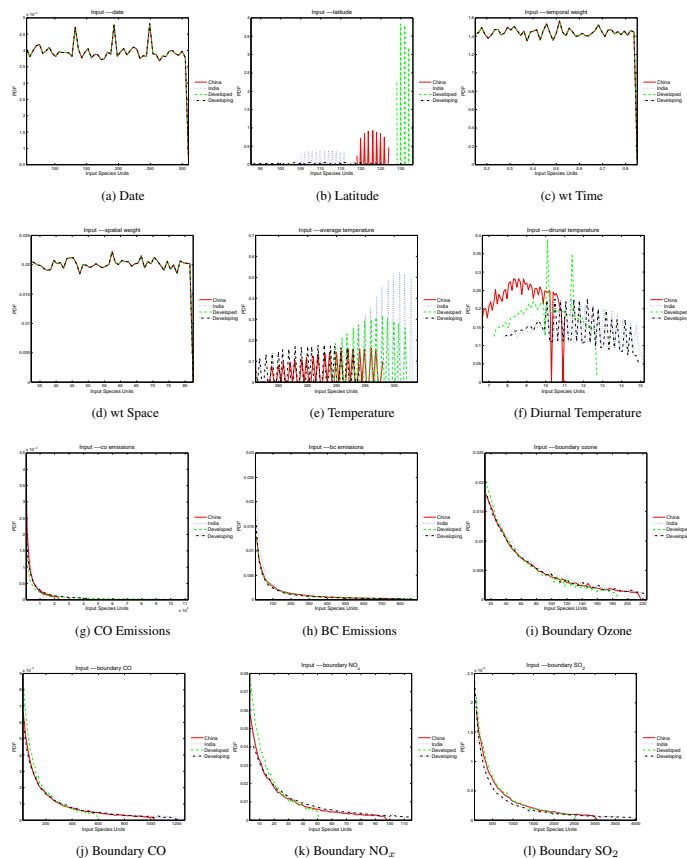


Fig. 5. These are the PDFs of 12 of the 13 required input species for 50 000 runs of the meta-model. Each input was randomly chosen to correspond to the inverse CDF of each PDF in the range from 0.15 through 0.85. The underlying PDFs, their units, and their best fit parameters are defined in Table 2. The reason that isoprene is not included is because it is the same as the underlying PDF given in Fig. 1

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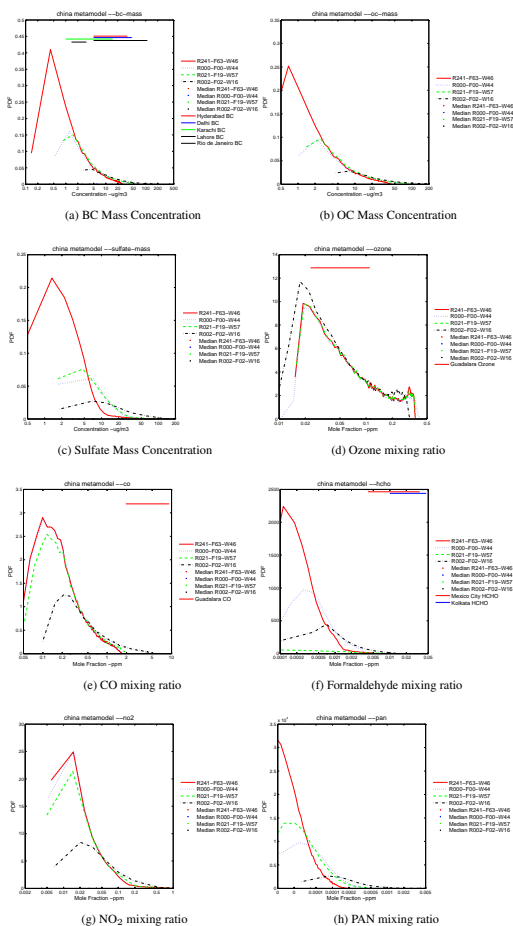
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Fig. 6. These are the PDFs of the total urban area mixing ratios of gases (ppm) and aerosol mass concentrations $\mu\text{g m}^{-3}$, from the China metamodel. For inputs, please refer to Fig. 5

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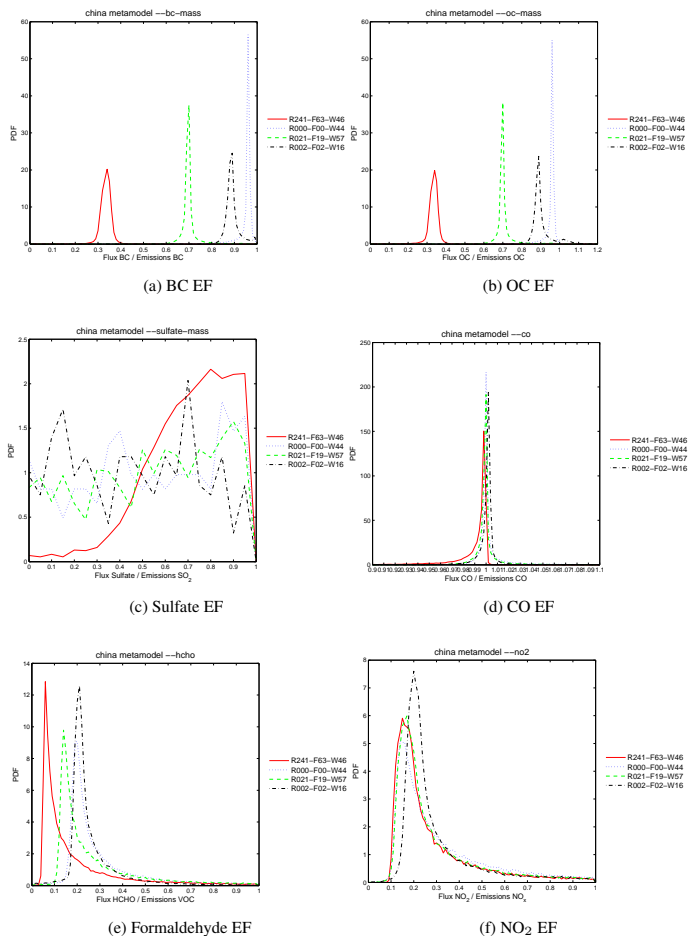


Fig. 7. These are the PDFs of the total urban area EFs, from the China metamodel. For inputs, please refer to Fig. 5.

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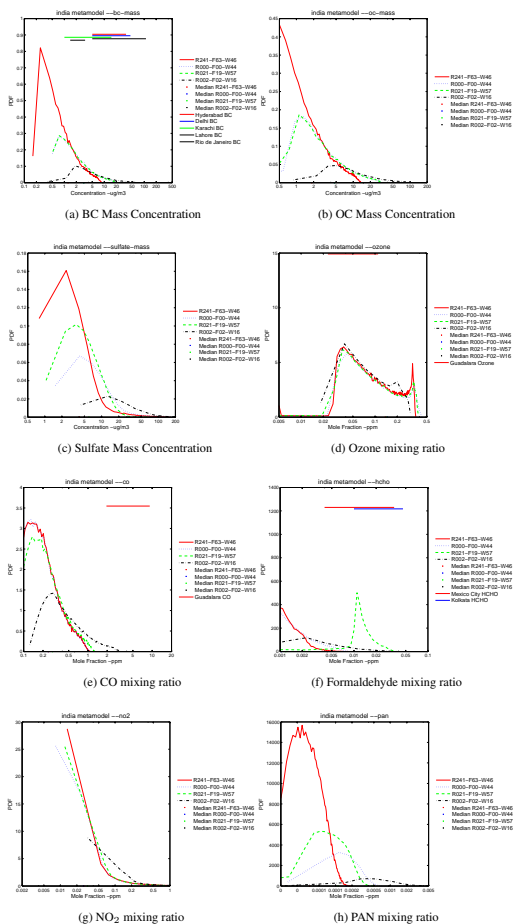
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Fig. 8. These are the PDFs of the total urban area mixing ratios of gases (ppm) and aerosol mass concentrations $\mu\text{g m}^{-3}$, from the India metamodel. For inputs, please refer to Fig. 5.

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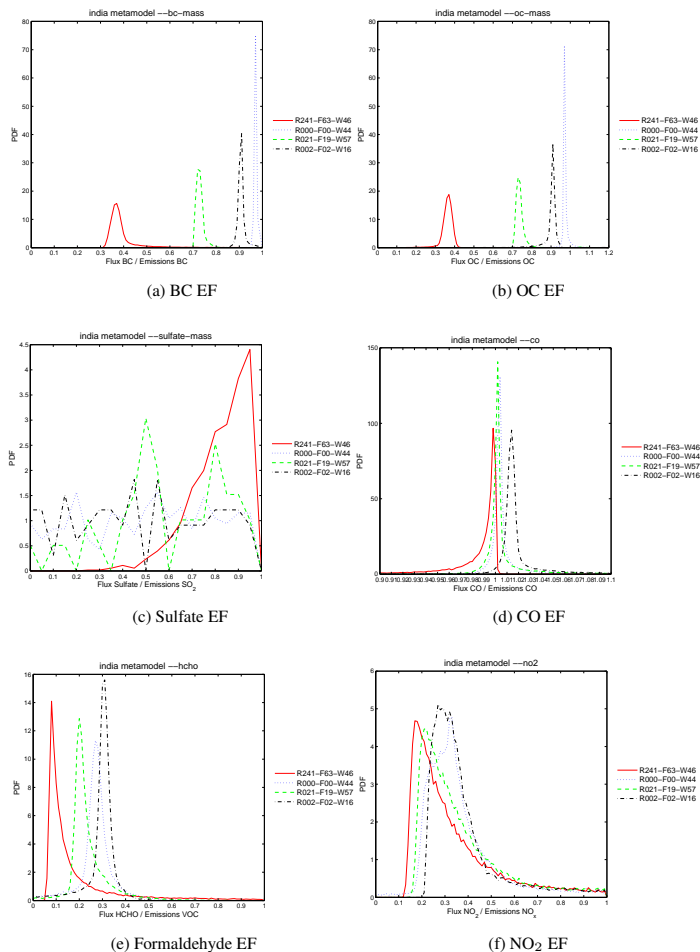


Fig. 9. These are the PDFs of the total urban area EFs, from the India metamodel. For inputs, please refer to Fig. 5.

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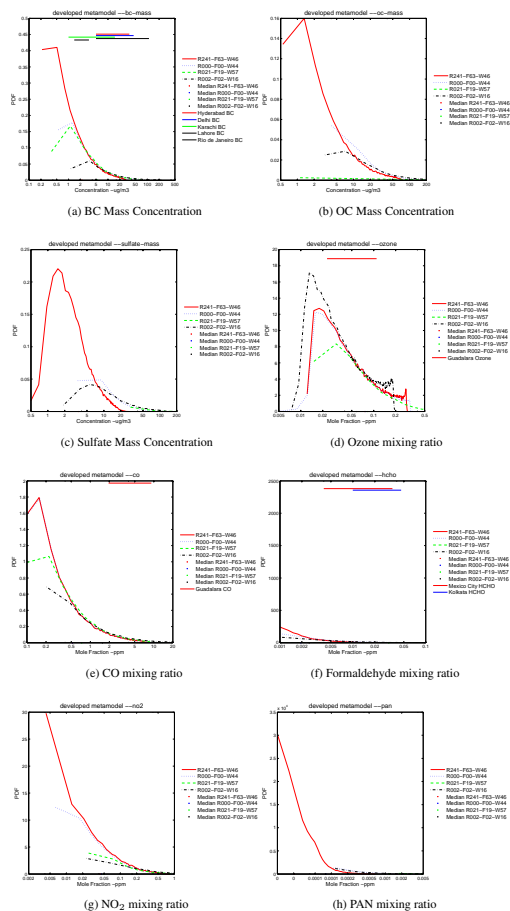


Fig. 10. These are the PDFs of the total urban area mixing ratios of gases (ppm) and aerosol mass concentrations $\mu\text{g m}^{-3}$, from the developed metamodel. For inputs, please refer to Fig. 5.

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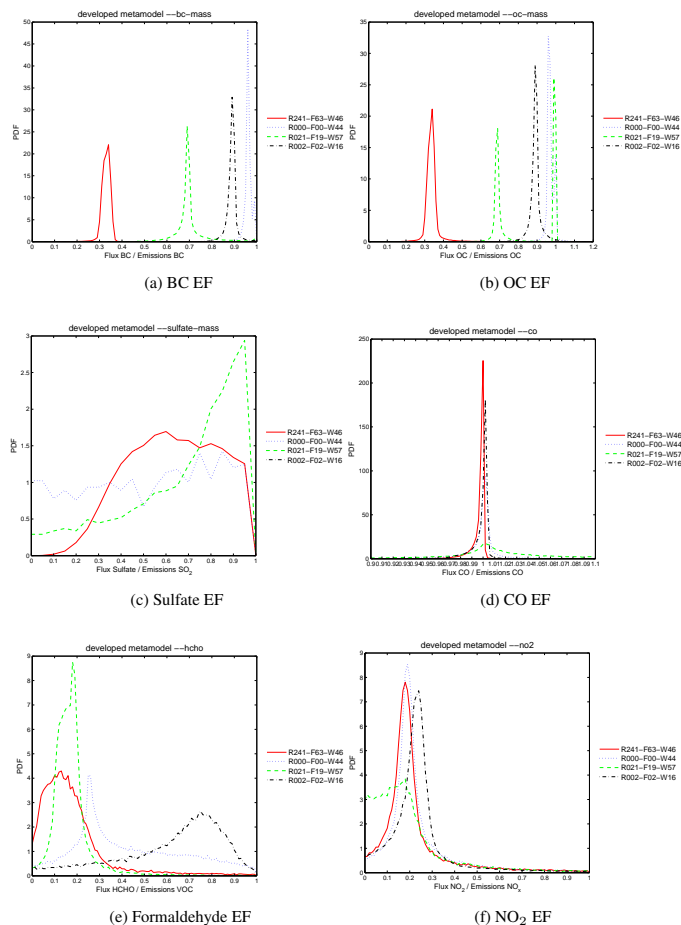


Fig. 11. These are the PDFs of the total urban area EFs, from the developed metamodel. For inputs, please refer to Fig. 5.

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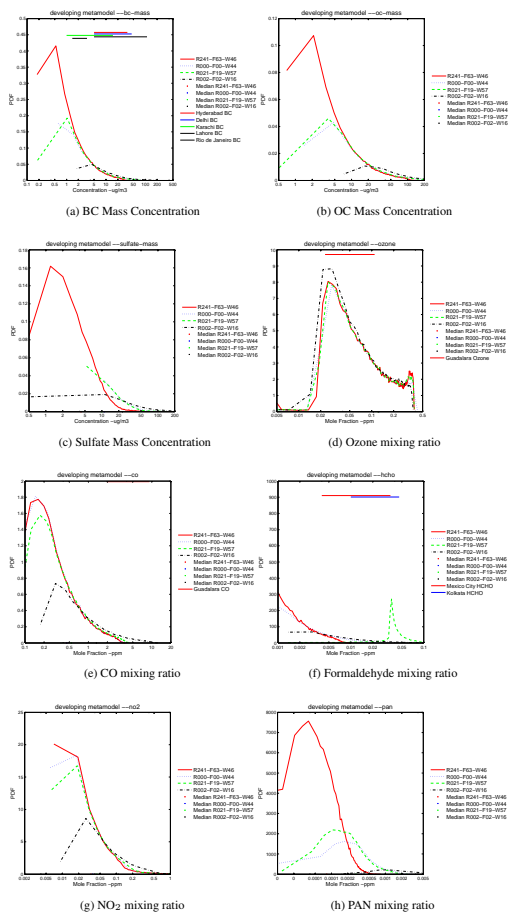


Fig. 12. These are the PDFs of the total urban area mixing ratios of gases (ppm) and aerosol mass concentrations $\mu\text{g m}^{-3}$, from the developing metamodel. For inputs, please refer to Fig. 5.

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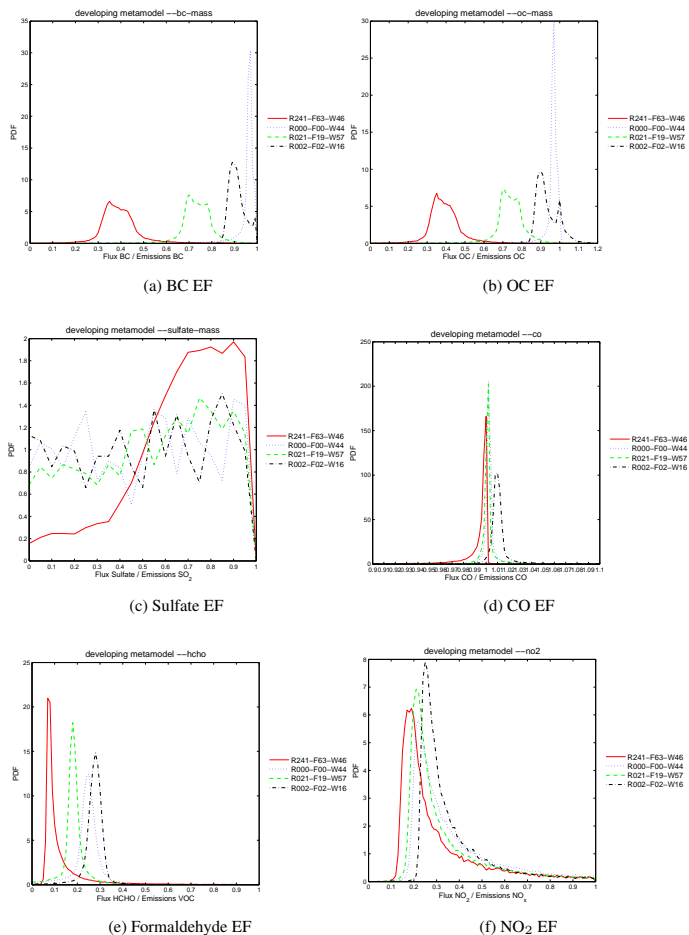


Fig. 13. These are the PDFs of the total urban area EFs, from the developing metamodel. For inputs, please refer to Fig. 5.

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